

RESEARCH ON ULTRA-HIGH-TEMPERATURE MATERIALS -  
MONOLITHIC CERAMICS, CERAMIC MATRIX COMPOSITES,  
AND CARBON /CARBON COMPOSITES

T. J. Miller and H. H. Grimes  
NASA Lewis Research Center  
Cleveland, Ohio

## TRENDS IN HIGH-TEMPERATURE MATERIALS

Efficiency in heat engines is directly related to the maximum allowable operating temperatures of the materials used in the hot section of the engine. The impetus to increase engine efficiency and performance has led to continuing improvements in material use temperatures. Figure 1 shows the increase in material use temperatures over the past three decades for superalloys used for turbine blades. Today's high-temperature superalloys can be used at temperatures up to approximately 2000° F without cooling. With cooling and the application of thermal barrier coatings, the superalloy operating temperatures can be increased somewhat. However, to permit significant increases in operating temperatures, new classes of materials will be required.

The Lewis Research Center (Lewis) is conducting research on three classes of materials that show potential for significant increases in operating temperatures. Another common advantage of these materials is that they contain readily available raw materials. These materials, monolithic ceramics, ceramic matrix composites, and carbon/carbon composites, are defined as follows:

Monolithic ceramic: a brittle, high-strength, refractory material composed of metallic and nonmetallic atoms. The materials being studied at Lewis are silicon carbide and silicon nitride.

Ceramic matrix composite: a ceramic matrix reinforced with high-strength ceramic filaments. The composites being studied at Lewis are silicon-carbide-reinforced silicon nitride, graphite, and silicon-carbide-reinforced oxide glasses.

Carbon/carbon composite: a carbon matrix reinforced with a carbon or graphite filament. The reinforcements can be either single-filament yarns or a woven cloth.

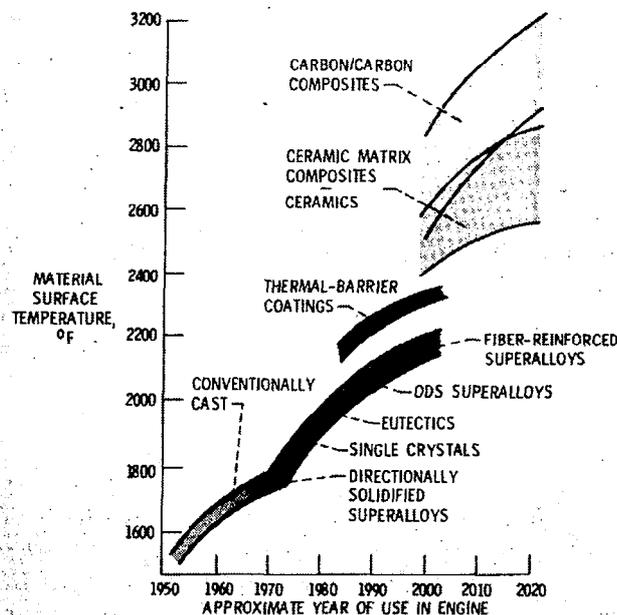


Figure 1

## OVERVIEW OF ULTRA-HIGH-TEMPERATURE MATERIALS

The three classes of materials discussed in this paper offer the common advantages of the potential for significant increase in operating temperatures and the use of readily available materials. They also have other potential benefits and liabilities, which are summarized in figure 2.

Of the three materials discussed in this paper, the most work has been done on monolithic ceramics. Research on monolithic ceramics has been conducted for many years and several development programs have fabricated parts for engine testing made of these materials (refs. 1 to 3). The most recent efforts to develop ceramic components for heat engines are the Department of Energy-sponsored Ceramic Applications in Turbine Engines (CATE) and Advanced Gas Turbine (AGT) projects, which are managed by Lewis (refs. 4 to 12). The work to date on monolithic ceramics has shown that these materials have good high-temperature strength and good oxidation resistance, but they are brittle and currently have low reliability. Improving the reliability is the major challenge for monolithic ceramic materials. The range of maximum operating temperatures for monolithic ceramics is 2400° F to 3000° F.

Ceramic matrix composite materials show the potential for improved toughness while maintaining good high-temperature strength and oxidation resistance. The major challenge with ceramic matrix composites is the fabrication of a dense body with uniformly distributed fibers that results in the desired material properties. Despite considerable interest in these materials, they are still in very early stages of research. The maximum operating temperature for ceramic matrix composites is projected to be approximately 3000° F (ref. 13).

Carbon/carbon composite materials offer the potential for good strength and toughness at very high temperatures (up to 4500° F) (ref. 14). These materials also have a very low density, less than 25 percent of the density of superalloys and 50 percent of the density of monolithic ceramics and ceramic matrix composites. The major challenges associated with these materials are reduction of the long and costly processing times currently required and development of improved ways of oxidation prevention.

MATERIAL TYPE	MAJOR POTENTIAL BENEFITS	MAJOR LIABILITIES	MAXIMUM OPERATING TEMPERATURE
MONOLITHIC CERAMICS	GOOD HIGH TEMPERATURE STRENGTH OXIDATION RESISTANCE	BRITTLINESS LOW RELIABILITY	2400°F TO 3000°F
CERAMIC MATRIX COMPOSITES	GOOD HIGH TEMPERATURE STRENGTH TOUGHNESS OXIDATION RESISTANCE	FABRICATION	3000°F
CARBON/CARBON COMPOSITES	GOOD STRENGTH AT VERY HIGH TEMPERATURE TOUGHNESS LOW DENSITY	OXIDATION FABRICATION	4500°F

Figure 2

## STATUS OF MONOLITHIC CERAMIC MATERIALS

Research on monolithic ceramic materials has been under way for many years (ref. 1). During this time, these materials have demonstrated many desirable characteristics (refs. 2 and 3); some of these are listed in figure 3. The major drawback of monolithic ceramic materials is low reliability. Two curves are shown in figure 3 which compare the reliability of today's monolithic ceramic materials and metals. In each case, the curves represent a typical strength distribution for these materials. For the metal, shown as a dashed line, a narrow range of strengths is indicated. Correspondingly, the strength of each component of the metal varies slightly from the average strength of the sample. One measure of this deviation in strength is the Weibull modulus( $m$ ). A high Weibull modulus corresponds to a material with a small strength deviation from the average. A Weibull modulus typical for a metal is approximately 40.

The distribution of strengths for current monolithic ceramics is represented in figure 3 as a solid line. The strength of each component of this material varies widely from the average strength of the sample. The Weibull modulus for current ceramic materials is approximately 10, which corresponds to a low material reliability. The low reliability results from a combination of the inherent brittleness of the material and the inclusion of very small flaws (20 to 50 $\mu$ m) in the material that can initiate failure. These flaws are introduced into the material as inclusions, voids, or surface defects during the processing of the material. The improvement of reliability is the focus of the Lewis research effort for monolithic ceramic materials.

### **CERAMIC MATERIALS HAVE DEMONSTRATED:**

- \* GOOD HIGH TEMPERATURE STRENGTH**
- \* GOOD OXIDATION RESISTANCE**
- \* GOOD EROSION RESISTANCE**
- \* NET SHAPE FABRICATION CAPABILITY**

### **BUT**

- \* LOW RELIABILITY**

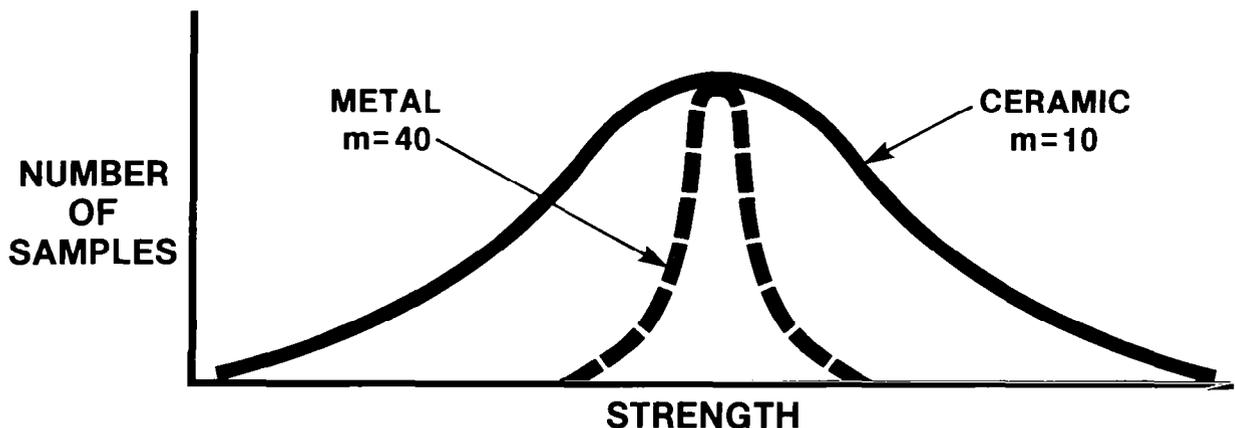


Figure 3

## MONOLITHIC CERAMIC MATERIAL PROCESSING

A simplified diagram for the processing of monolithic ceramic materials is shown in figure 4. These materials require an ultra-fine (submicrometer size particle) starting powder. This powder is currently obtained by grinding or milling coarser commercial powders (e.g., silicon carbide or silicon nitride) until the required particle size is achieved. Sintering additives are required in the processing of these materials to achieve a fully dense final part. These additives must be thoroughly blended with the starting powders. Typical sintering aids for silicon nitride are refractory oxides (i.e., yttria); aids for silicon carbide are boron and carbon.

To make a part or shape of this material, several processes can be applied to form a green (unsintered) body. Some of the processes currently being used to make parts of ceramic materials are isopressing, injection-molding, and slip-casting. Parts can also be made by hot-pressing, but they usually require considerable grinding to achieve final shape; this process can be very expensive.

The next step in processing is densification of the green body to a fully dense part. Two of the processes that are used for densification are sintering and hot isostatic pressing (HIPing). Sintering is the application of high temperature to densify the part. Hot isostatic pressing is the application of both high temperature and very high pressure to densify the part. During this densification process a linear shrinkage in the part of approximately 17 percent (typical for sintered material) can result. The result of these process steps is a fully dense monolithic ceramic body.

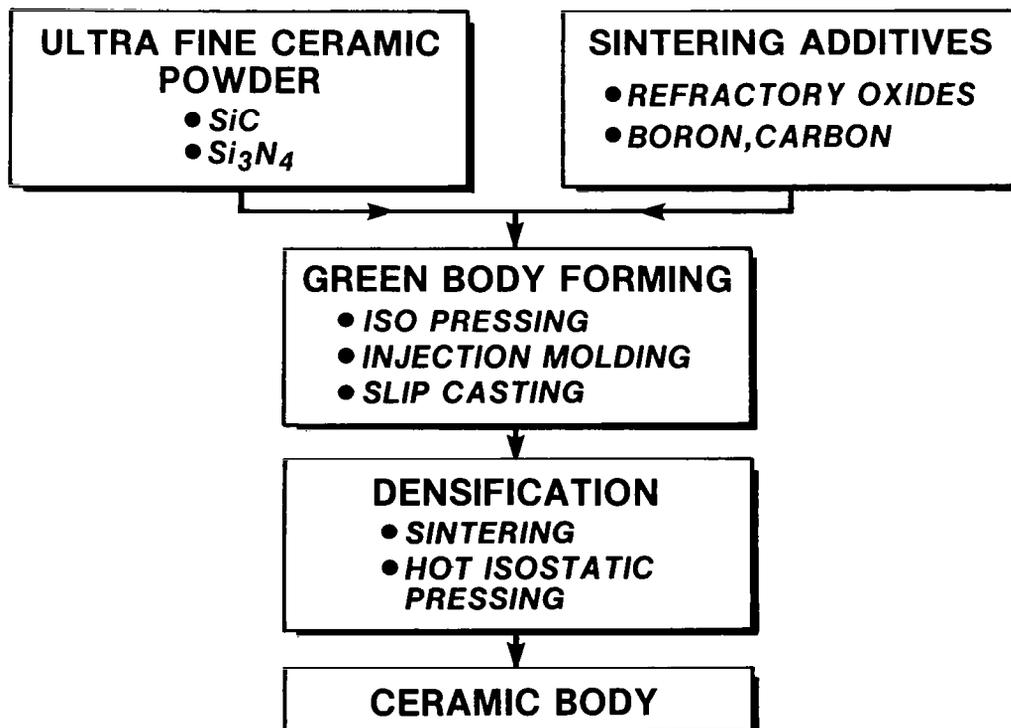


Figure 4

LEWIS MONOLITHIC CERAMIC RESEARCH PROGRAM

The objective of the Lewis Monolithic Ceramics Research Program is to develop technology for ceramic materials with improved reliability by understanding the interrelationships between starting powder, densification process, microstructure, and properties. This program is shown schematically in figure 5. The materials included in the program are sintered silicon carbide (SSC), sintered silicon nitride (SSN), and sintered-reaction-bonded silicon nitride (SRBSN). The major emphasis in the program is densification; however, the program also includes powder processing, nondestructive evaluation, and material evaluations.

Starting powders and sintering aids are obtained from commercial sources and are ground and blended together to achieve an ultra-fine powder with uniformly distributed sintering aids. Test bars are prepared and processed through one of the two densification processes selected for study - hot isostatic pressing (HIPing) and high N<sub>2</sub> pressure sintering. Each of these densification processes will be further described later in this paper. Nondestructive evaluation of the test bars is performed at selected steps in the processing to identify the source of flaws introduced into the bars. Selected material evaluations (strength, microstructure evaluation, distribution of strength, and fractographic analysis) are then conducted to determine the effect of changes in processing parameters on the fully dense ceramic test bars.

This program is iterative and provides feedback at each processing step to identify the most significant parameters that affect the reliability of monolithic ceramic materials.

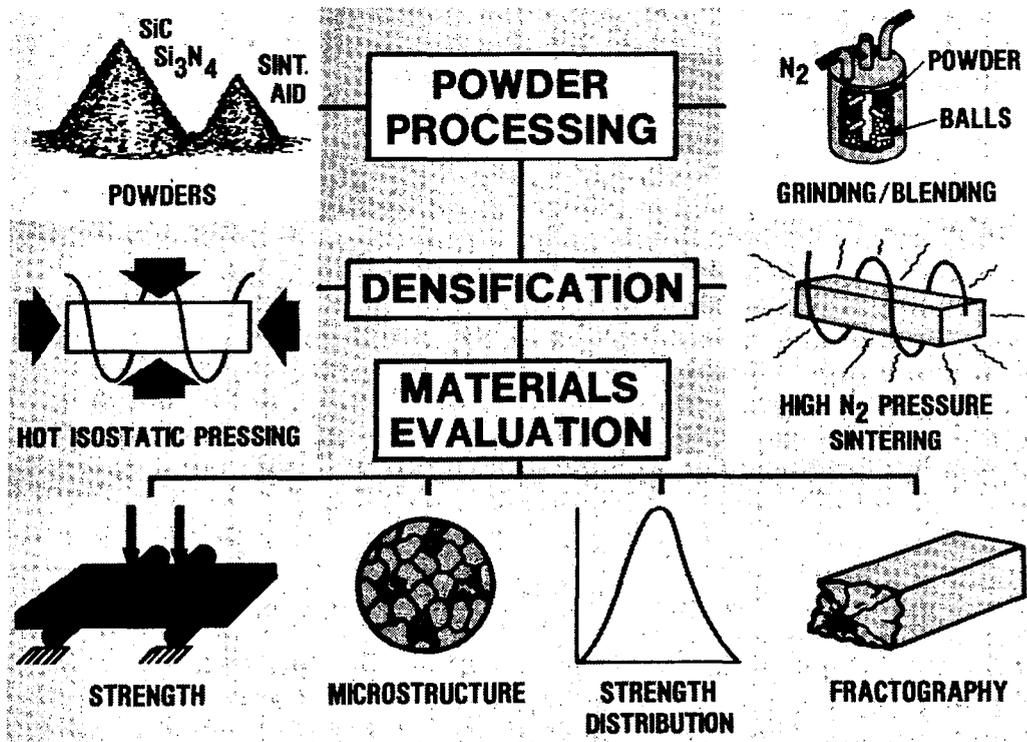


Figure 5

## LEWIS MONOLITHIC CERAMIC RESEARCH APPROACHES TO DENSIFICATION

As discussed earlier, densification is the major emphasis of the Lewis Monolithic Ceramics Research Program. The two approaches to densification in the program are HIPing and high  $N_2$  pressure sintering. Lewis has facilities, shown in figure 6, for conducting both of these densification processes.

HIPing is a process that uniformly applies very high temperatures and pressure to the part being processed. The Lewis HIP unit has been designed to operate at the very high temperatures necessary for ceramic materials. The unit is capable of a maximum operating temperature of  $3990^\circ F$  and a maximum operating pressure of 20 000 psi using argon gas as the pressure medium. HIPing studies are being conducted on SSC and SRBSN. The results of the early HIPing studies conducted to date at Lewis are presented in reference 15.

High  $N_2$  pressure sintering is a process that uniformly applies nitrogen pressure and very high temperatures to the part being processed. The Lewis high  $N_2$  pressure sintering unit is capable of up to 1000 psi nitrogen pressure and  $3720^\circ F$  temperature. This process is particularly effective for silicon nitride materials because it permits higher sintering temperatures and lower levels of sintering aids to be used.

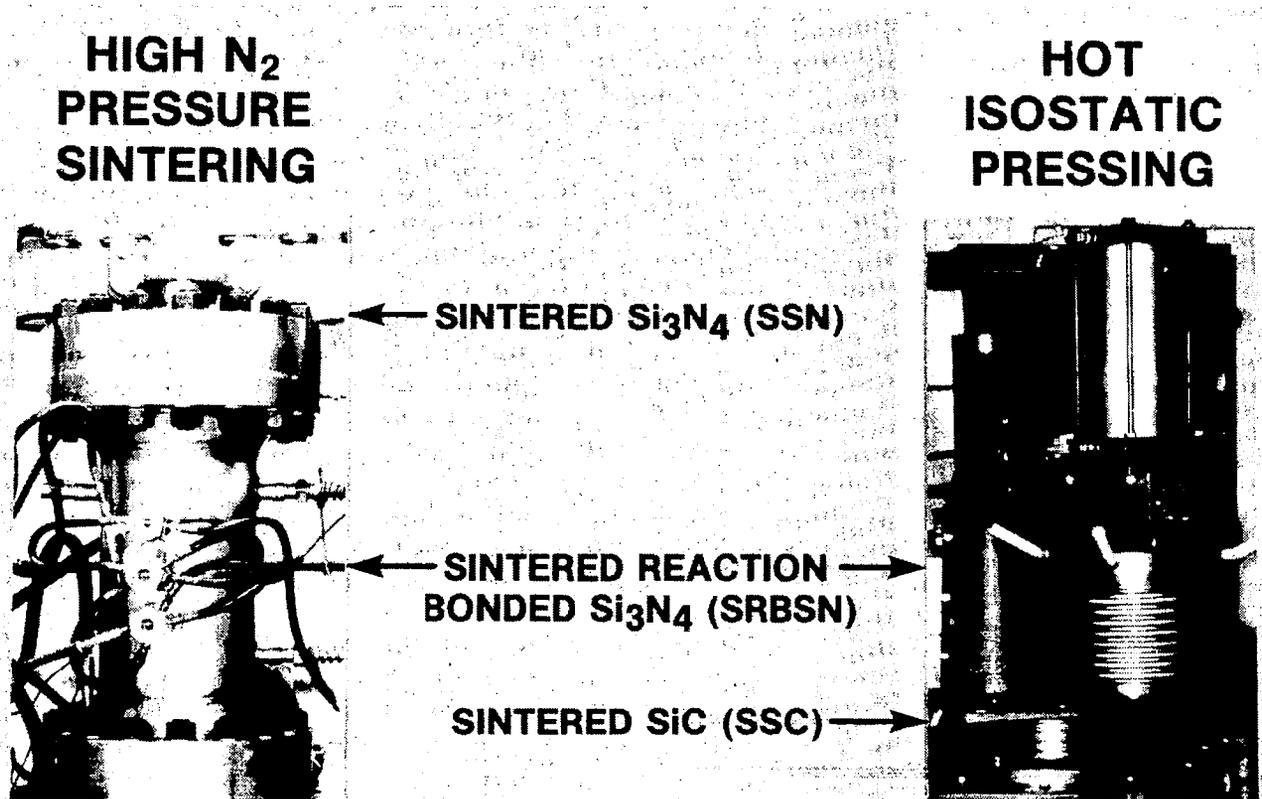
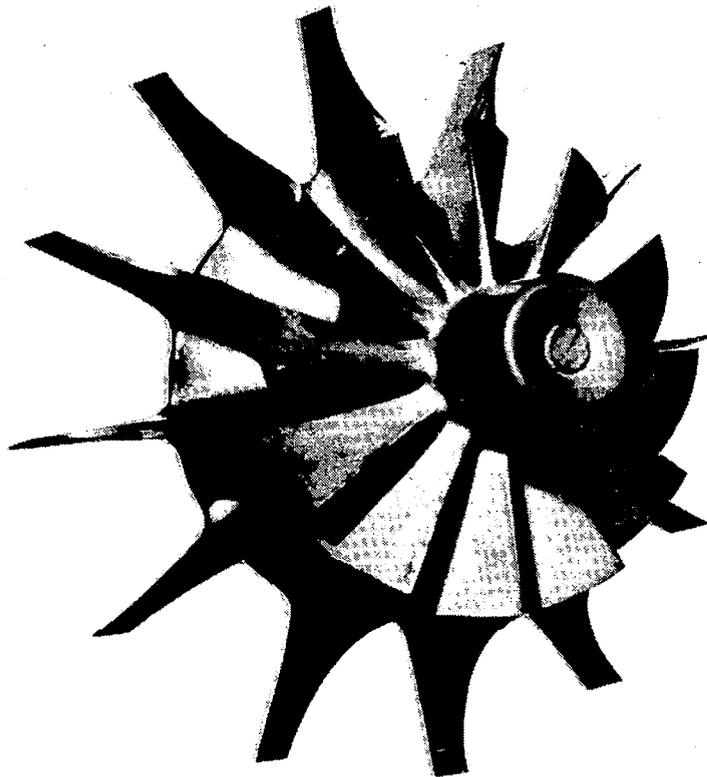


Figure 6

## MONOLITHIC CERAMIC RADIAL TURBINE ROTOR

Monolithic ceramic gas turbine components are currently being developed in the CATE and AGT projects (refs. 4 to 12). As an example of current fabrication technology, figure 7 shows a ceramic radial turbine rotor that was made for this project by the Carborundum Company. This rotor is designed for a 100 hp automotive gas turbine engine. This 6-inch-diameter rotor is made of sintered silicon carbide by injection-molding and meets the final dimensional specifications (blade shape, blade thickness, tolerances, etc.) in the as-sintered state. Ceramic turbine rotors are also being developed for the AGT project by AiResearch Casting Company, Ford Motor Company, and GTE Laboratories.



## SINTERED ALPHA SILICON CARBIDE

Figure 7

## STATUS OF CERAMIC MATRIX COMPOSITES

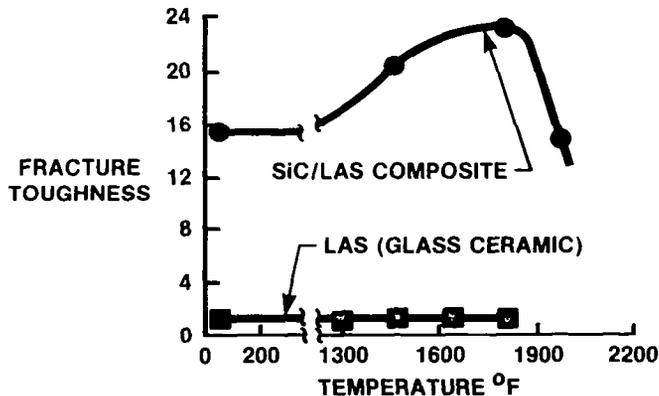
Although monolithic ceramics offer potential for use in oxidative environments at high temperature, their brittleness may limit their use in certain structural applications. A promising approach to improving the toughness of brittle materials is reinforcement with fine filaments or fibers. The fibers contribute both to increased strain-to-failure of the material and to limited growth of fatal cracks. The success of this approach has recently been demonstrated by glass ceramic matrix composites produced by the United Technologies Research Center (ref. 13). These composites, which are comprised of lithium aluminum silicate (LAS) glass ceramic reinforced with silicon carbide fibers, show a nearly 10-fold improvement in fracture toughness over the unreinforced ceramic (fig. 8). The units of fracture toughness are  $\text{ksi} \times \sqrt{\text{in.}}$  in this figure. This improvement extends to temperatures over  $2000^\circ \text{F}$ , above which temperature the composite's utility is limited by the softening of the LAS glass ceramic.

Attempts to reinforce higher temperature ceramics have not been so successful (ref. 16), primarily due to fiber strength degradation related to:

1. fiber/matrix interactions at the higher fabrication temperatures;
2. recrystallization of the reinforcing fibers at these temperatures;
3. fiber fracture due to processing-induced abrasion and stresses.

### CERAMIC MATRIX COMPOSITES OFFER—

- ★ **HIGH TEMPERATURE CAPABILITY**
- ★ **OXIDATION RESISTANCE**
- ★ **IMPROVED TOUGHNESS**



**BUT, HIGHER TEMPERATURE CERAMIC MATRIX COMPOSITES DEGRADE DURING FABRICATION DUE TO—**

- ★ **FIBER/MATRIX INTERACTIONS**
- ★ **FIBER RECRYSTALLIZATION**
- ★ **MECHANICAL TRAUMA**

Figure 8

## STATUS OF CARBON /CARBON COMPOSITES

Carbon/carbon composites have shown good strength and toughness over an even wider temperature range (ref. 14). This material, however, which has a composition similar to a piece of coal, must be protected in oxidizing environments (fig. 9). Generally, this protection is achieved through the use of ceramic coatings. But, in applications where catastrophic oxidation of a component due to a failed coating would be intolerable, the oxidation rate may be retarded by the incorporation of oxidation-inhibiting materials into the matrix. Another major problem with carbon/carbon composites is the long repetitive processing required to prepare dense materials. These process times can exceed 800 hours and contribute significantly to the cost.

For both carbon/carbon and ceramic matrix composites, designs for optimum strength and toughness have not been possible because the fracture mechanisms and effects of composite parameters are poorly understood. The Lewis research program to study these composites addresses this problem, as well as the problems of fabrication, oxidation, and thermal stability.

### **CARBON/CARBON COMPOSITES OFFER—**

- \* GOOD STRENGTH AT VERY HIGH TEMPERATURES**
- \* TOUGHNESS**
- \* LOW DENSITY**

### **BUT, PRESENT PROBLEMS WITH**

### **CARBON/CARBON INCLUDE—**

- \* OXIDATION**
  - NEEDS COATINGS
  - INTRINSIC OXIDATION RESISTANCE
- \* FABRICATION**
  - LONG/REPETITIVE PROCESSING TO ACHIEVE DENSITY

Figure 9

HIGH TEMPERATURE NONMETALLIC COMPOSITE FABRICATION

A better understanding of the Lewis program may be gained by reviewing the fabrication processes of the two composite materials (fig. 10). Reinforcing filaments of silicon carbide, alumina, and carbon are all currently being prepared commercially from polymer precursors using conventional fiber-spinning plus a pyrolysis step. These small-diameter, high-strength filaments are flexible and can be spun and woven into yarn, cloth, or other preform shapes. Matrix materials in powder or gel forms, or precursor materials which can be converted to the final matrix material, can be introduced into the preforms at relatively low temperatures. The matrix is then densified either by sintering, hot-pressing, or chemical conversion of a precursor to a higher temperature material. However, because carbon melts at such a high temperature, the only practical method of preparation of a carbon matrix is by pyrolysis of a precursor. If extensive shrinkage occurs during the pyrolysis process, the infiltration/densification cycle will have to be repeated to obtain a dense composite body. This repetition, of course, contributes significantly to the processing time required.

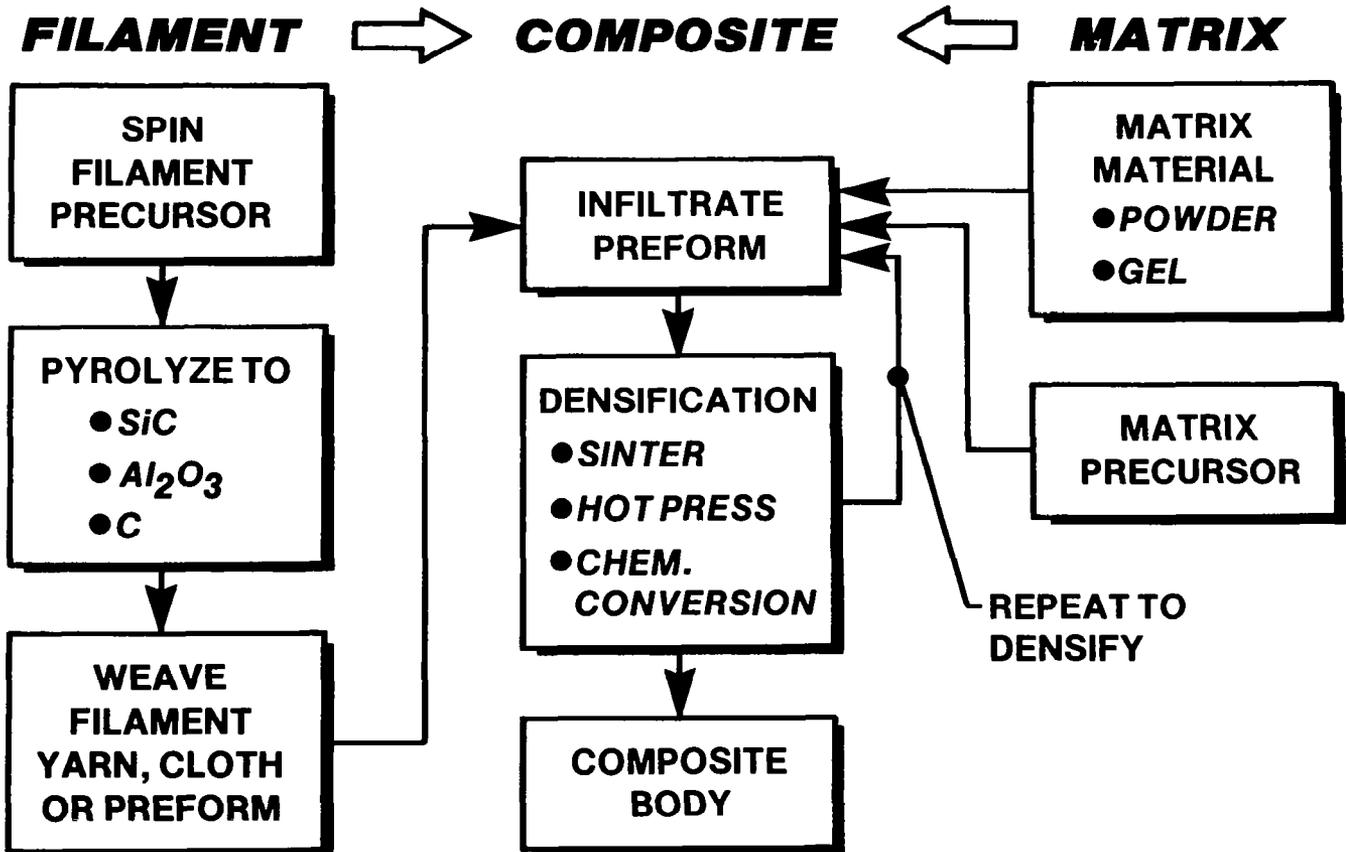


Figure 10

LEWIS CARBON/CARBON AND CERAMIC MATRIX COMPOSITES RESEARCH PROGRAM

The Lewis carbon/carbon research program (fig. 11) seeks to reduce processing time and cost through development of more processible matrix precursors with improved char yields. The approach here is to find ways to prepare condensed carbon ring structures through more extensive in-situ crosslinking at lower temperatures. In addition, we will attempt to make these composites more oxidatively stable by incorporating oxidation inhibitors into the matrix through the use of modified polymer precursors. These inhibitors do not replace the need for coatings on the carbon/carbon structure, but rather they inhibit rapid oxidation if the coating should fail. Another research group in the Materials Division at Lewis is studying the coatings problem.

In our ceramic matrix composites program, we again address the processibility problem. The goal here is to fabricate silicon carbide filament-reinforced silicon nitride matrix composites via lower temperature methods. One approach is to produce silicon nitride by in-situ pyrolysis of polymer (Si-N)<sub>n</sub> compounds which have been deposited in a filament preform. Pyrolysis should occur at temperatures well below those at which degradation occurs between filament and matrix. This approach should also eliminate the traumatic effects of pressing. However, as with carbon/carbon composites, this processing may require repeated infiltration and densification to achieve a dense matrix. A second approach involving somewhat higher processing temperatures (but still below those required for hot pressing or sintering ceramics) involves the reaction of a porous silicon powder matrix with nitrogen to form silicon nitride. This reaction has been studied by ceramists at Lewis since it is also used to prepare monolithic reaction-bonded silicon nitride (refs. 17 and 18).

Another major element of the program is the study of the fracture behavior of brittle filament/brittle matrix composites. Few guidelines exist to help in the design of a carbon/carbon matrix composite for optimum strength and toughness. Our approach here is a systematic study of the fracture behavior of both classes of composites to determine the effects of the materials' properties, component size and geometry, and composite design. With this knowledge, we will develop analytical models which will permit optimization of composite strength and toughness. Computer models designed originally to provide similar understanding of metal matrix composites (ref. 19) are presently being modified to aid in this task.

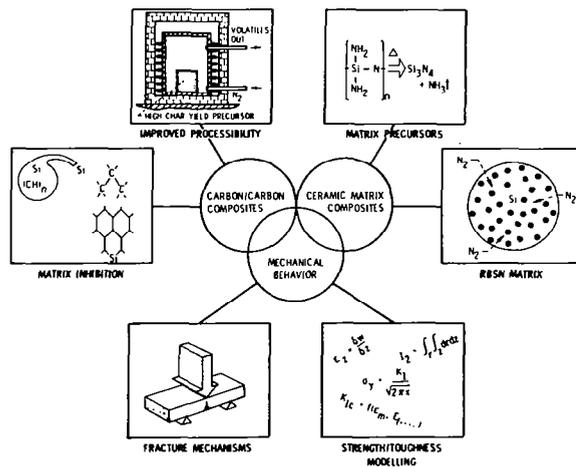


Figure 11

## CARBON/CARBON COMPOSITES

An example of the state of the art in carbon/carbon composite applications is shown in figure 12. This figure shows a prototype carbon/carbon component made by General Electric Co. (private communication). The component is a one-piece bladed turbine rotor which, in service, would have to be coated to prevent oxidation. At the lower left is a representative coated carbon/carbon microstructure showing the reinforcing filaments aligned in several directions. At the top of this figure, the silicon carbide oxidation coating can be seen.

Other gas turbine engine applications for which carbon/carbon composites are being studied include exhaust nozzle flaps and seals, augmenters, combustors, and acoustic panels.

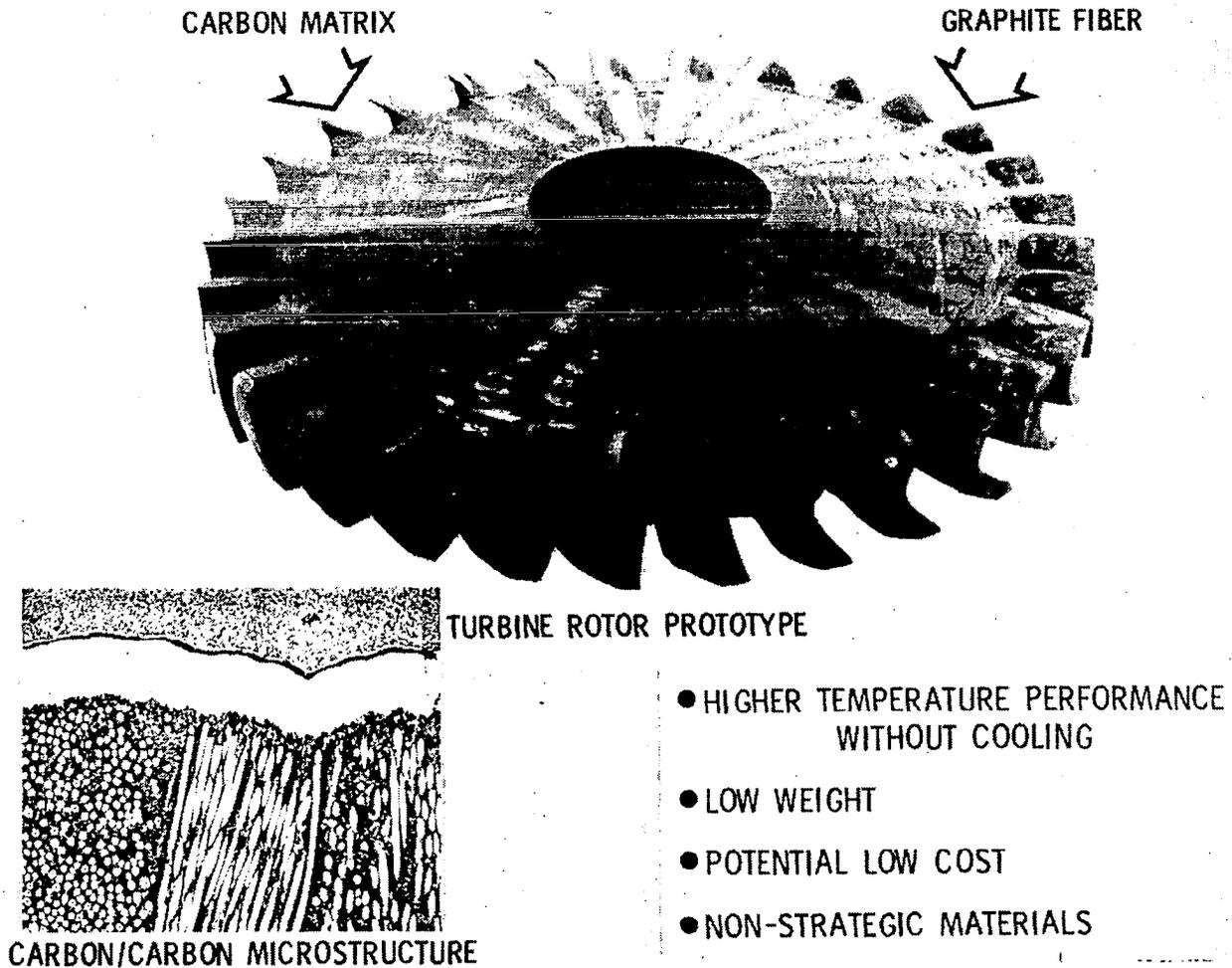


Figure 12

## CERAMIC MATRIX COMPOSITES

The ceramic matrix composite technology is less developed than the carbon/carbon technology. The most mature ceramic matrix composite is probably the silicon carbide filament-reinforced glass ceramic (LAS) composite of United Technologies (ref. 13). This material is currently being considered for several applications in both the aerospace and automotive industries. The coupon shown in figure 13 is being studied for use in a divergent seal in the exhaust section of a gas turbine engine. This reinforced glass ceramic shows a factor of 2 to 5 times improvement in strength, and a factor of 4 to 10 times improvement in toughness over unreinforced glass ceramic. The improved toughness may be due, in part, to the fiber pullout seen in the fracture surface at the lower left.

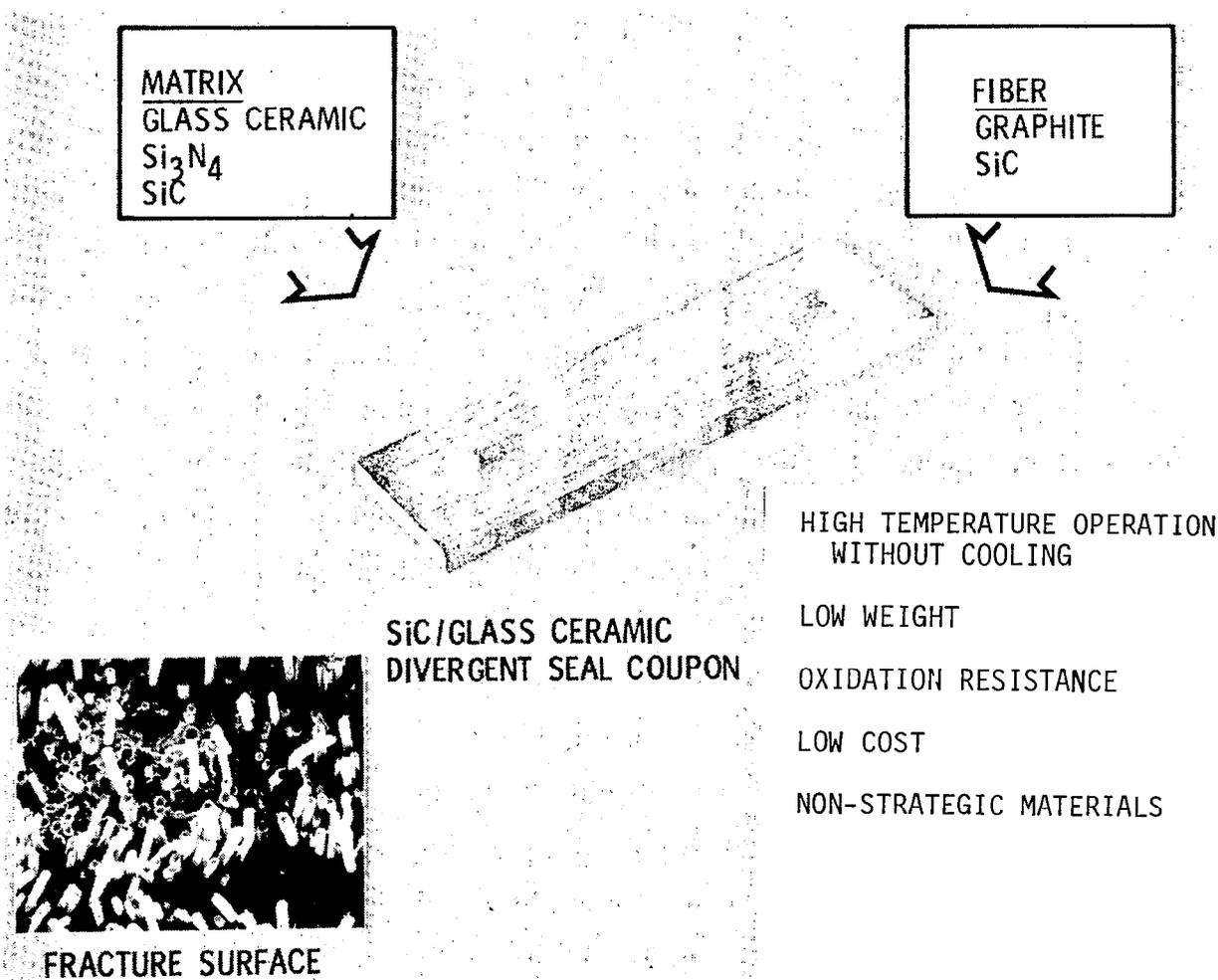


Figure 13

## CONCLUDING REMARKS

Monolithic silicon carbide and silicon nitride, silicon-carbide-reinforced silicon nitride composites, and coated carbon/carbon composites offer potential as very-high-temperature structural materials for a variety of aerospace and terrestrial applications. The Lewis research program focuses on the key challenges that must be met to realize the potential benefits of these materials. Application of these materials will improve the efficiency and performance of heat engines, while reducing the requirements for strategic materials in superalloys.

## REFERENCES

1. Rice, R. W.: An Assessment of the Use of Ceramics in Heat Engines. NRL Memorandum Report 4499, 1981.
2. Katz, R. N.: Ceramics for Vehicular Engines: State of the Art. AMMRC MS 80-2, 1980.
3. McLean, A. F.: Ceramic Technology for Automotive Turbines. Ceramics Bulletin, vol. 61, no. 8, 1982, pp. 861, 865, 871.
4. Hudson, S. M.; et al.: Ceramic Applications in Turbine Engines. Progress Report for Period 1, July 1979 to 31 December 1979. (Detroit Diesel Allison; NASA Contract DEN3-17). NASA CR-159865, 1980.
5. Byrd, J. A.; et al.: Ceramic Applications in Turbine Engines. Progress Report for Period 1, January 1980 to 30 June 1980. (Detroit Diesel Allison; NASA Contract DEN3-17). NASA CR-165197, 1980.
6. Rackley, R.; et al.: Advanced Gas Turbine (AGT) Powertrain System Development for Automotive Applications. Progress Report Number 1 (October 1979 - June 1980). (AiResearch Manufacturing Company of Arizona; NASA Contract DEN3-167). NASA CR-165175, 1980.
7. Helms, H. H.; et al.: Advanced Gas Turbine (AGT) Powertrain System Development for Automotive Applications. First Semiannual Report (October 1, 1979 - June 30, 1980). (Detroit Diesel Allison; NASA Contract DEN3-168). NASA CR-165178, 1981.
8. Helms, H. H.; et al.: Advanced Gas Turbine (AGT) Powertrain System Development. Second Semiannual Report (July 1, 1980 - December 31, 1980). (Detroit Diesel Allison; NASA Contract DEN3-168). NASA CR-165504, 1981.
9. Rackley, R.; et al.: Advanced Gas Turbine (AGT) Powertrain System Development for Automotive Applications. Second Semiannual Progress Report (July 1980 - December 1980). (Garrett Turbine Engine Company; NASA Contract DEN3-167). NASA CR-165329, 1981.
10. Byrd, J. A.; et al.: Ceramic Applications in Turbine Engines. Progress Report for Period 1, July 1980 to 31 December 1980. (Detroit Diesel Allison; NASA Contract DEN3-17). NASA CR-165494, 1981.
11. Helms, H. H.; et al.: Advanced Gas Turbine (AGT) Power Train System Development. Third Semiannual Report (January 1, 1981 - June 30, 1981). (Detroit Diesel Allison; NASA Contract DEN3-168). NASA CR-165504, 1981.
12. Helms, H. H.; et al.: Advanced Gas Turbine (AGT) Power Train System Development. Fourth Semiannual Report (July 1, 1981 - December 31, 1981). (Detroit Diesel Allison; NASA Contract DEN3-168). NASA CR-167875, 1982.

13. High Temperature Metal and Ceramic Matrix Composites for Oxidizing Atmosphere Applications. National Materials Advisory Board Report, NMAB-376, 1981.
14. Delmonte, J.: Technology of Carbon and Graphite Fiber Composites. Van Nostrand Reinhold Company, New York, 1981.
15. Watson, G. K.; and Moore, T. J.: Hot Isostatic Pressing of Structural Ceramics at NASA. To be published in the Nineteenth Summary Report of Automotive Technology Contractor's Coordination Meeting, October 1982.
16. Fairbanks, J. W.; and Rice, R. W.: Proceedings of the 1977 DARPA/NAVSEA Ceramic Gas Turbine Demonstration Engine Program Review. Battelle Metals and Ceramics Information Center, MCIC-78-36, 1977.
17. Herbell, T. P.; and Glasgow, T. K.: Developing Improved Reaction Sintered Silicon Nitride. 15th Summary Report of DOE Highway Vehicle Systems Contractors, CONF-781050, 1979.
18. Herbell, T. P.; Glasgow, T. K.; and Shaw, N. J.: Reaction Bonded Silicon Nitride Prepared from Wet Attrition - Milled Silicon. Ceramic Engineering and Science Proceedings, vol. 1, no. 7-8(B); 1980. (Also published as NASA TM-81428.)
19. Adams, D. F.; and Murphy, D. P.: Analysis of Crack Propagation as an Energy Absorption Mechanism in Metal Matrix Composites. Tech. Rep. UWME-DR-101-102-1, Univ. of Wyoming, Dept. of Mech. Eng., 1981.